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by T. Spalvins and D. H. Buckley
Lewis Research Center
Cleveland, Ohio

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Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio

ABSTRACT

Various vacuum deposition methods are used to deposit soft, thin metal gold films on metal surfaces for lubrication purposes. When a metal film is deposited on a surface, the adhesion characteristics of the deposited metal film to the substrate depend on the type and structure of the interfacial region. This interfacial region is directly related to the solid solubility and alloying concepts. The type or nature of the interface directly influences the endurance and strength properties of a lubricating film. Three vacuum deposition methods were used here: (1) vapor deposition, (2) sputtering and (3) ion plating. The characteristics of the film and interface were examined in friction experiments in ultra high vacuum. The coefficient of friction was used to determine the strength and durability of the deposited film. Depending on the vacuum deposition method and the selection of film and substrate material, five types of interfaces can be distinguished. The diffusion and high energy embedded interfaces are desirable because a graded, layer-like interface is formed.

INTRODUCTION

Various vacuum deposition methods may be used for depositing films and coatings on metal surfaces for a number of uses and applications. The surface is the entrance to the solid, and the nature of the interface between

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the substrate and the film is of great importance in many areas (friction, lubrication, wear, adhesion, cold welding, thermal shock resistance, erosion, corrosion etc). An interface is a discontinuity, and it has an energy state higher than the continuum which it bounds. Energy of the atoms at the interface would depend strongly upon the efficiency of the packing and hence of bonding to their neighbors. The interface is always a site of disturbance, on an atomic scale, since atoms in the interface do not have the same regular arrangement as they have in the interior of the phase. In solids, grain boundaries, interphase boundaries, twin boundaries etc. are considered as a type of interface. When a metal film is deposited on a surface, the adhesion and interfacial characteristics of the deposited film to the substrate depend primarily on:

1. Cleanliness of the substrate (should be atomically clean)
2. Substrate and film materials
3. Method of film deposition
4. Temperature of the substrate during deposition

All of these factors contribute to formation of a particular type, structure and bonding forces across an interfacial region.

The objective of this investigation was to define the five types of interfaces developed in the deposition of their metallic films by the various vacuum deposition methods, and determine how these interfaces effect the film strength and durability during friction experiments.

In this study, thin gold films of about 1800Å were deposited by 3 different vacuum deposition methods (vapor deposition, sputtering, ion plating). These deposited gold films were used as solid film lubricants for rotating or

sliding components to reduce the coefficient of friction and reduce probability of complete seizure of the moving parts. The strength and durability of the film is extremely critical to lubrication, and these two film parameters are directly related to the type and structure of the interfacial region. Thus, the type and nature of the interface formed is directly related to friction and lubrication, namely to the strength and durability of the lubricating film. The characteristics of the film and interface were examined in friction experiments in ultra high vacuum, using a hemispherical niobium rider sliding on a disk specimen to which the film had been applied. The coefficient of friction is an indication of the strength and durability of the film and also to some extent the depth and type of the interfacial region. Depending on the selection of the film and substrate material and the type of vacuum deposition method, five types of interfaces can be distinguished and related to the strength and durability of the film as a lubricant.

APPARATUS

Ultra-High Vacuum Friction Apparatus

The vacuum friction apparatus (fig. 1) is used for determining the coefficient of friction for the coatings deposited by the various vacuum deposition methods. The basic components of the apparatus are the test specimens, 2-1/2 inch diameter flat disk and 3/16-inch-radius rider. The disk specimen is mounted on the end of the horizontal shaft in the vacuum chamber. Against the disk, a 3/16 inch hemispherical rider specimen is loaded. The rider is held in place by a rigid arm which projects through a port in the side of the vacuum chamber. A removable gimbal assembly, which is used to load the rider against the disk surface and to monitor the frictional force through a strain-gage assembly. The friction test is

conducted in a vacuum of 10^{-11} torr and the pressure monitored by a cold-cathode (Kreisman) vacuum gage.

VACUUM DEPOSITION APPARATUS

The three vacuum deposition techniques (vapor deposition, sputtering and ion plating) are performed in a vacuum chamber (bell jar). The pumping system consists of a mechanical pump, three stage oil diffusion pump, and a liquid-nitrogen baffle. The chamber can be evacuated to a pressure of 10^{-6} to 10^{-7} torr.

Deposition Methods

In this investigation 3 vacuum deposition methods were selected:

1. Vapor deposition (fig. 2)
2. Sputtering (fig. 3)
3. Ion plating (fig. 4)

In all these methods, the substrate surface was cleaned in vacuum (electron bombarded or argon ion bombarded) before depositing the film. These vacuum deposition methods form a film which is in intimate contact with the substrate; it intimately conforms to the contours of all surface irregularities. The material used for deposition in all instances was gold (99.999 percent).

Since gold is a relatively soft metal with no affinity for oxygen, it forms stable low shear strength films when bonded to hard substrates and thereby functions as a solid film lubricant. The film thickness was in the order of 1800Å and was measured by an interference microscope or directly during deposition by the oscillating quartz crystal monitor.

<u>Vapor Deposition</u>. - This method (fig. 2) is most commonly used for film preparation (ref. 1). It may be defined as condensation of an element or compound from the vapor state to form solid deposits (films). Prior to

deposition of gold, the substrate was cleaned by electron bombardment (thermally etched) in high vacuum.

Sputtering. - This technique (fig. 3) is generally performed in an argon atmosphere of several microns, and a potential is applied across the electrodes to ionize the gas (refs. 2, 3). The material to be sputtered is made the cathode (the target) and the positive ions from the gaseous plasma are accelerated toward the cathode. These highly excited ions have sufficient energy to knock off or sputter atoms from the surface of the target. The sputtered atoms are redeposited on the substrate which is placed close to the target surface.

Ion Plating. - This method of applying films (fig. 4) is a very recent method (refs. 4, 5). Basically, the process consists of simultaneous sputtering and ion deposition. A gas discharge is established between the cathode (substrate material) and the anode (evaporant source and filament). A potential of 3-5KV is applied across the two electrodes in an argon atmosphere of about 20 microns of mercury. The ionized positive argon ions are accelerated toward the cathode and sputtering takes place. While sputtering takes place, the plating material on the filament is heated to evaporation and the evaporated metal atoms are ionized in the plasma and accelerated toward the substrate with a high velocity, thus depositing to form a film. To obtain a film, it is important that the rate of deposition be higher than the rate of sputtering. Depending on the potential across the electrodes the metal ions can be physically imbedded below the surface.

RESULTS AND DISCUSSION

As already stated there are four basic parameters which affect adhesion and which in turn affect the interface: cleanliness, materials, method of

deposition and temperature. The significant differences among these three vacuum deposition methods with respect to the interface formation will be considered in the selection of the substrate and film material and in the energy considerations of the metal atoms or ions. In vapor deposition techniques, the depositing atoms have only thermal energy, approximately 0.1 to 1.0 electron volts (ref. 5). In sputtering the sputtered atoms may have energies in the order to 100 electron volts (ref. 5). In ion plating, the ionized material has the highest energy, and the metal ions are physically driven below the surface. Depending on the potential across the electrodes, the penetration depths can be selectively controlled.

In film formation with vapor deposition, nucleation first takes place at selected surface sites which is followed by the formation of a continuous film (ref. 6). With films deposited by sputtering and ion plating, a continuous film forms immediately, without nucleation (ref. 6).

Types of Interfaces

Depending on the cleanliness of the substrate, selection of materials, vacuum deposition methods and temperature of the substrate during deposition, 5 types of interfaces can be distinguished:

1. Physical
2. Mechanical
3. Intermetallic compound
4. Diffusion
5. High energy embedment

Physical Interface. - This type may be described as one which has mainly van der Waals forces across it (ref. 7). This type of interface is formed when there is no diffusion between the film and substrate material. This

interface may be considered as an abrupt, sharp line, thus confined to a very narrow region.

Mechanical Interface. - This interface is sometimes referred as having a keying effect. The film material fills the rough areas and forms a mechanical interlocking. There is no chemical reaction between the film and substrate. Due to the distinct lattice mismatch, large strains are present and disparity in the coefficient of thermal expansion must be expected. Films which were formed with physical and mechanical interfaces by vacuum deposition have essentially no effect on reducing the coefficient of friction. The films have very poor adherence and fail immediately when tested in friction experiments. Figure 8 shows that films which have physical and mechanical interfaces and when tested in friction experiments the film is immediately broken at the start of the experiment. The coefficient of friction starts almost at the same value[1,2] as for the bare metal without a lubricant. The interface in both of these types is very abrupt (fig. 5). It does not have a graded or transition layer between the film and the substrate. Thermal stress and coefficient of expansion effects are maximum in such an interface. In lubrication systems this type of interface is undesirable. This foregoing discussion applies to vacuum deposited film. Where film transfer is developed due to mechanical action (e.g. rubbing) physically or mechanically bonded films may afford surface protection in lubrication applications.

Intermetallic Compound Interface. - This interface is formed when the film and substrate metals differ sufficiently in electrochemical properties. The film and substrate materials react to form well defined compounds and such compounds are totally different than the parent metals and are usually brittle and friable. Electronegativity of an element or metal is a measure of its tendency to accept valence electrons and, therefore, the relative electronegativities indicate qualitatively whether a new phase is likely to form and the nature of the bonding in this phase. This intermetallic phase usually occurs at definite atomic ratios (stoichiometric) and most often exhibits a narrow homogeneity range. Due to the incompatibility of this phase, with the parent metals and its non-plastic nature, this interface is also undesirable for lubrication applications. A typical example of this type of interface is formed in the (Al-Au) binary system. If a gold film is vapor deposited on an aluminum substrate at about 220° C, a brittle purple phase forms which has been identified as $AuAl_2$ (refs. 8, 9). The initial formation of the purple $AuAl_2$ intermetallic compound during vapor deposition of gold on aluminum substrate at 260° C and 220° C is shown in figures 6 and 7 respectively. A distinct phase change occurs with the formation of the intermetallic compound $AuAl_2$ which has a distinct purple color. With continued evaporation of gold, this purple color gradually changes to a light lavender color before the gold film completely covers the surface as shown by the gold color. It is interesting to note that it is not necessary to have a liquid in order to form gold aluminum intermetallic compounds. This reaction occurs at relatively low temperatures during vapor deposition

as indicated in figures 6 and 7. This interface also has a narrow distance over which the transition takes place, thus being again sensitive to the internal stresses and differences in the coefficient of thermal expansion between the intermetallic compound and the substrate. This interface may be avoided in the selection of the film and substrate metal systems, namely selecting systems which do not form intermetallics.

Diffusion Type Interface. - In diffusion bonding, the principal process variables are temperature, pressure and time and these factors are usually influenced by surface preparation and condition. A diffusion type interface may be best explained by relating it to mutual solubility or alloying ability of the particular bi-metallic components. Factors which affect mutual solubility are atomic size, crystal structure, electrochemical activity, valency and types of forces that hold the atoms in their lattices (ref. 10). If these factors for the metals in a metallic system (film and substrate) are very similar, the requirements for mutual solubility are met and this is a perfect condition for diffusion to take place in the solid state. In this investigation, gold was deposited on a clean (Ni-Cr) surface at elevated temperature and a gold film was formed (ref. 1). Since the mutual solubility requirements are satisfied in this metallic system, a diffusion type interface was formed. This again was determined by the friction experiments (fig. 8). The strength and durability here was good due to the adhesion and bonding characteristics. The interatomic diffusion between the film and substrate forms a concentration gradient. This interdiffusion will continue until equilibrium is attained and until the bulk concentration in the interfacial region is homogeneous. Due to the concentration gradient between the film and substrate the internal strains and the coefficient of thermal

expansion are minimized. The friction curves (fig. 8) indicate that once the rider has worn thru the film, the coefficient of friction does not rise steeply but increases gradually and approaches the coefficient of friction for the substrate material. To obtain a diffusion bond, the two materials do not require complete mutual solubility but some degree of solid solubility or alloying is required.

High Energy Embedment. - This type of interface is formed during ion plating when a high potential is applied across the cathode and anode. The basic difference between the diffusion interface and this type of interface lies in the fact that solubility and alloying concepts which were the basis for the formation of the diffusion interface are not a requirement. This interface may be formed with a bi-metallic system where the two metals are dissimilar, namely having liquid immiscibility. Also an elevated temperature to supply the activation energy for diffusion is not required for the formation of this type of interface.

The high energy metal ions which are impinging on the substrate have sufficient energy to penetrate below the surface. The width and depth of the interfacial region formed is dependent on the material combination (relative masses of the metal ions and the substrate atoms) and the potential across the two electrodes. A typical value for the mean penetration of a heavy ion into a metal lattice is from 50Å/KEV to 150Å/KEV of ion energy (ref. 5). This method was used for depositing gold films on the (Ni-Cr) substrates. Friction tests (fig. 8) indicate that the coefficient of friction for a film formed using ion plating is lower than films formed by the other two methods.

The coefficient of friction is about 0.2 for a relatively long time (85 min.). Also, the strength and durability is improved over any of the

other two methods used in this study. As the film was broken, the coefficient of friction did not abruptly rise. As wear takes place, the coefficient of friction rises gradually, approaching the coefficient of friction of the substrate material; this result indicates the diffuse nature of the interface.

The data of figure 8 indicates that as a result of repeated friction experiments the films deposited by high energy embedment were markedly superior to films deposited by other two methods. They were superior in two respects: (1) they provided lower friction coefficients and (2) they had longer endurance lives.

SUMMARY OF RESULTS

The material combinations (film and substrate) selected and the particular vacuum deposition method used, has a pronounced effect on the strength and durability of a thin lubricant film. The strength and durability of a film is related to adhesion which in turn depends on the type of interface formed between the film and substrate. It was determined that the diffusion type and the high energy embedded type interfaces are the most desirable from the standpoint of friction and lubrication. In both cases there is a graded interface. For the diffusion type interface, mutual solubility and alloying should be present. However, in selecting the ion plating method, a graded interface can be obtained without considering solubility and alloying factors. In both cases a relatively wide transition type interface is formed, thus minimizing the internal stresses and the effects of differences in coefficient of thermal expansion, therefore, improving the strength and durability of the lubricating films. Friction results with these two interfaces showed the best results.

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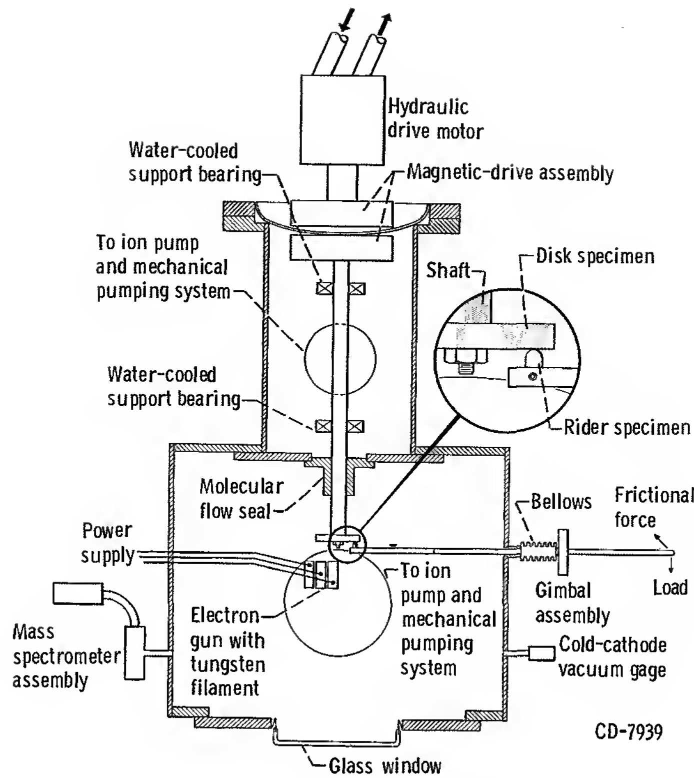

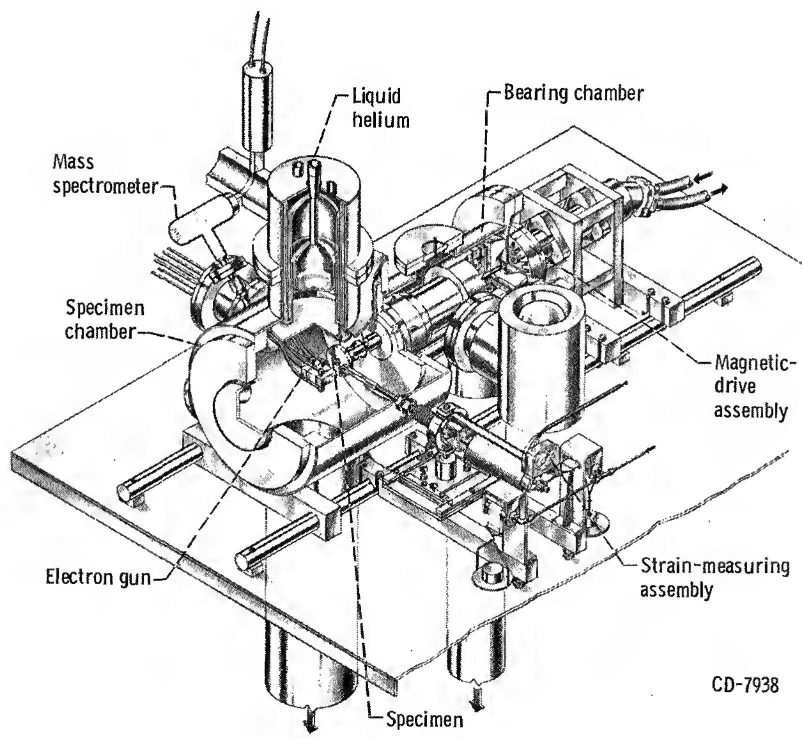

Figure 1. - Ultra-high-vacuum friction apparatus.

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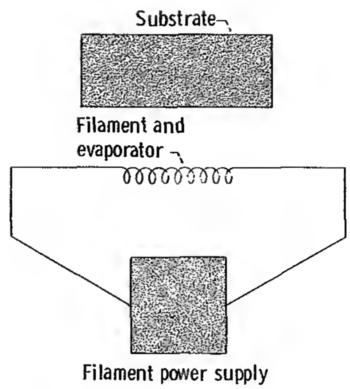

Figure 2. - Vapor deposition system.

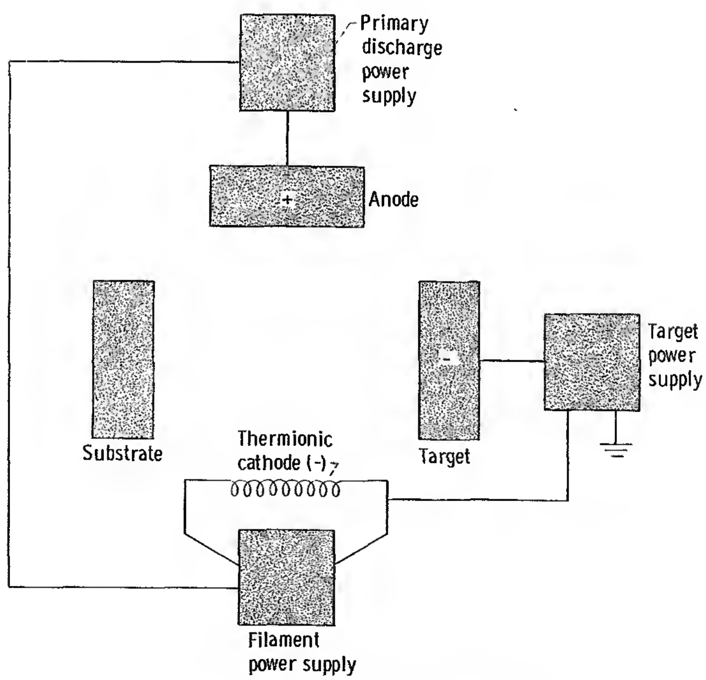

Figure 3. - Sputtering (Triode) system.

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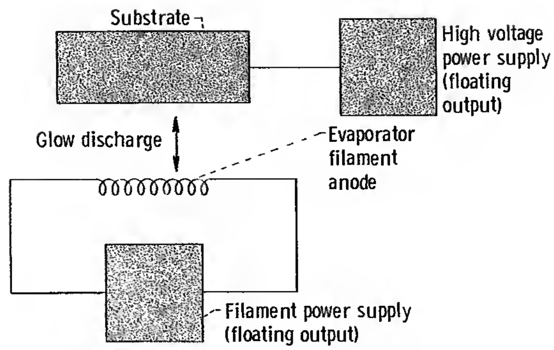

Figure 4. - Ion plating system.

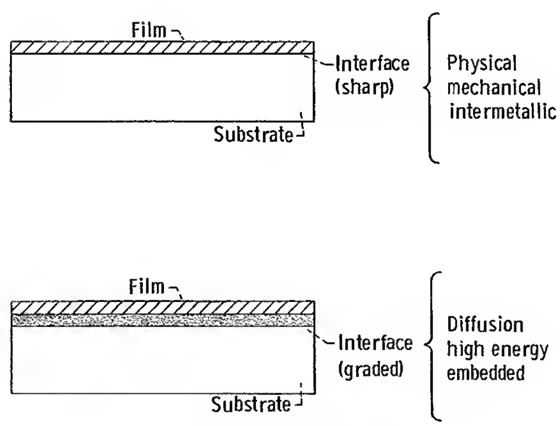

Figure 5. - Abrupt and graded interface.

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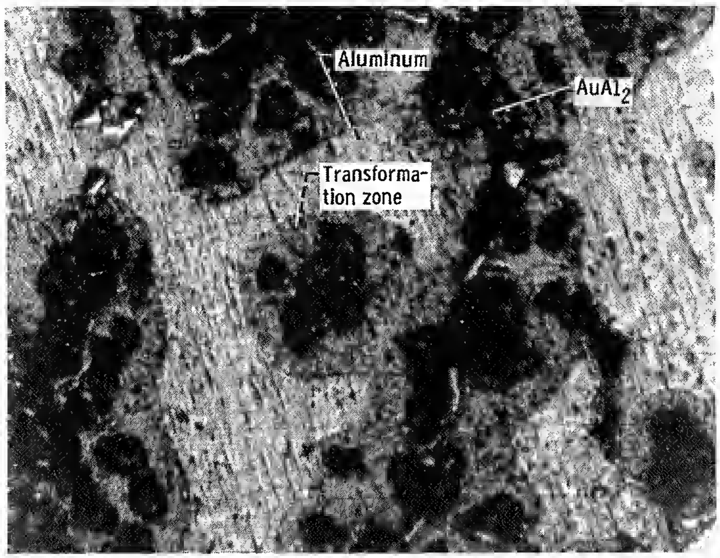

Figure 6. - Initial formation of purple $AuAl_2$ during vapor deposition of gold on aluminum surface at 260° C. X775.

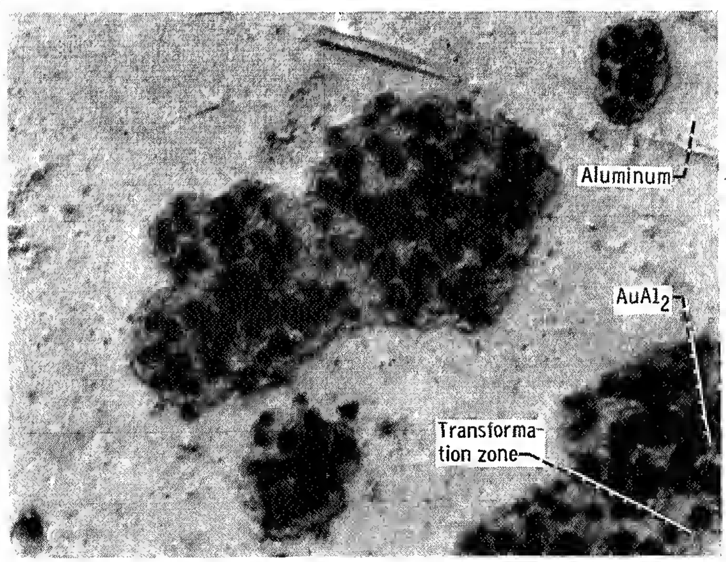

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Figure 7. - Initial formation of purple $AuAl_2$ during vapor deposition of gold on aluminum surface at 220° C. X925.

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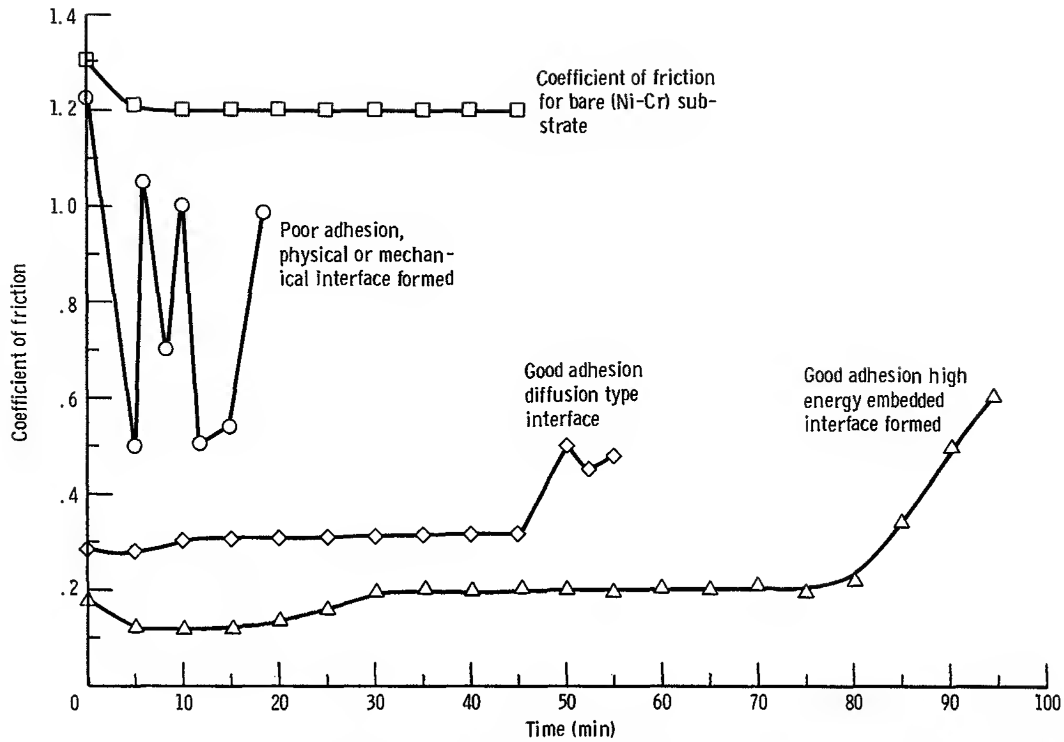

Figure 8. - Coefficient of friction of niobium sliding on (Ni-10 percent Cr) alloy with gold deposited film in vacuum, load 250 grams, speed 5 feet per minute, ambient temperature.